

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460



OFFICE OF CHEMICAL SAFETY AND
POLLUTION PREVENTION

MEMORANDUM

DATE: 19-MAR-2020

SUBJECT: **Sulfur Dioxide:** Review of "Measurement of Sulfur Dioxide Emissions as Related to Worker Exposures Resulting from Table Grape Packages Containing Sulfur Dioxide-Generating Paper Pads, Plastic Sheets, or Plastic Liners that are used to Preserve Table Grapes"

PC Code: 111409

Decision No.: 543321, 556907

Petition No.: N/A

Risk Assessment Type: Study Review

TXR No.: N/A

MRID No.: 50971301

DP Barcode: D448360, D454962

Registration No.: N/A

Regulatory Action: Registration Review

Case No.: 4056

CAS No.: 7681-57-4

40 CFR: 180.444

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Purpose of Study

As part of the scoping document for the inorganic sulfites, HED identified a need for data to evaluate emission rates from commodities treated using sodium metabisulfite pads, and the potential for occupational exposure due to sulfur dioxide emissions in the channels of trade. Sodium metabisulfite pads are registered for use with both imported and exported grapes.

The Agency required a lab-based, product-specific, off-gassing study with simulated fumigation conditions. In 2014, a data call-in (DCI) was sent out requiring these data as part of registration review, and in response to that DCI, a study was initiated to examine the off-gassing of sulfur dioxide resulting from the use of sodium metabisulfite products. This submission presents the results of the study and aims to satisfy the following guidelines cited in the DCI: *Special Study SS-1117*.

Methodology

The study was conducted in three parts:

Experiment 1: This experiment was conducted to evaluate the differences in flux between various product types. A laboratory-scale evaluation of the flux of SO₂ from sodium metabisulfite product types (A through F; see Table 1 below) was conducted at a temperature of 63°F and relative humidity (RH) level of 80%. Six product types were evaluated for SO₂ emissions and flux in triplicate¹. The emission of SO₂ into headspace was measured in 8-L glass dynamic flow-through chambers housed in a walk-in environmental incubator with programmable temperature. Air samples were collected at 15-minute intervals over the time course of the experiment (which ranged from less than a day to 16 days depending on the product).

Table 1. Characteristics of the Various Sodium Metabisulfite Pad Product Types.

Product	Product Type	Release Type ¹	Use	Material	Size (cm; LxW)	Size (cm ²)	Sodium Metabisulfite (g)	Sodium Metabisulfite (ug)
A	Sheet	Dual	Import	Plastic	26x46	1196	6	6,000,000
B	Sheet	Dual	Import	Plastic	26x46	1196	4	4,000,000
C	Pad	Dual	Import	Paper	26x46	1196	7	7,000,000
D	Bag	N/A	Import and Export	Plastic	40x60	2400	7	7,000,000
E	Sheet	Single	Export	Plastic	26x46	1196	6	6,000,000
F	Pad	Single	Export	Paper	26x46	1196	7	7,000,000

1. Dual release pads include both a quick and slow release phase, while single release pads only have one release phase.

Experiment 2: A pilot-scale evaluation of flux from a 3-box load of packed grapes subject to a simulated import scenario was evaluated over three weeks of storage/transport at 32°F and 85% RH. The flux of SO₂ was evaluated under four different scenarios: (1) sodium metabisulfite pad only, (2) pad + box (no grapes), (3) pad + grapes (no box) and (4) pad + grapes + box (typical real-world scenario). The set-ups were placed inside 5 ft³ chambers housed in a temperature controlled-atmosphere room for 21 days. SO₂ concentrations were measured at 100-minute intervals over the time course of each experiment. Only product type C (a dual release pad) was used for this experiment; this product type resulted in the highest flux from experiment 1. The experiment was conducted for 21 days at 32°F followed by 4 days at 40°F (consistent with pending methyl bromide fumigation at US ports).

Experiment 3: A commercial-scale evaluation of flux from 88-box pallets of packed grapes was conducted following the same procedures as in the pilot-scale study. A pallet containing a single product and packaging type was transferred to a 1000 ft³ controlled-atmosphere room and SO₂ concentrations were measured. SO₂ concentrations were measured at 15-minute intervals over the time course of each experiment which ran from 11 to 31 days depending on the product type. The experiment was conducted at 32°F.

¹ It is unclear if the experiment with product B was conducted in triplicate since only one set of results for that product was reported in the raw data provided.

Results

Experiment 1: The study authors reported that SO₂ emissions were reproducible for each table grape packaging material, however, key differences were noted across packaging types (see Table 2 and Figures 1 and 2 below). In general, greater fluxes of SO₂ were emitted for longer periods of time from paper pads relative to the plastic sheets, however, the plastic sheets reached maximum flux relatively quicker. The single release pads reached a maximum flux faster but then stayed at a relatively stable emission rate while the dual release pads reached a maximum flux a little slower and then decreased and then reached a pseudo-steady state flux. Figures 3 through 8 provide representative SO₂ emission profiles for the various product types.

Experiment 2: For experiment 2, product C, a dual release pad, was used to evaluate the influence of packing materials and grapes on the emission of SO₂. Product C was chosen since it was found to result in the highest flux in Experiment 1. The addition of packing material (boxes) as well as grapes were found to greatly impact the flux of SO₂, with a reduction of approximately 16X from just the pads themselves to a set up of the pads, grapes and boxes (Table 3 and Figure 9). It was also found that over the last 10 days of the experiment, the average SO₂ emission from the scenario consisting of grapes, pads and boxes was approximately 69 ppbv (Figure 10).

Experiment 3: The results of Experiment 3 indicated that all SO₂ concentrations were below the method LOD (100 ppb) following the use of SO₂-generating products to treat pallets of table grapes in both the import and export scenario on a commercial scale. The study authors note that further studies would need to be done with methods that allow for lower detection limits in order to measure the flux of SO₂ from treated grapes using sodium metabisulfite pads.

Discussion

The study report provided a summary of results from studies evaluating the levels of SO₂ in air after use of sodium metabisulfite pads to treat grapes. The results of Experiment 1 confirmed expected differences in flux from the various types of pads (e.g., single vs dual release, and paper vs plastic sheets). Both Experiments 2 and 3 indicated that concentrations of SO₂ from sodium metabisulfite pads are fairly low, staying around 1 ppm or lower during the Experiment 2 and falling below the LOD of 100 ppb for Experiment 3 study.

Conclusion

HED has reviewed the submitted study and found it acceptable for risk assessment purposes. The study provides relevant information related to potential for exposure to SO₂ following the use of registered sodium-metabisulfite pads. HED has determined that this submission satisfies the following requirement cited in the DCI: *Special Study SS-1117*.

Table 2. Summary of Results from Experiment 1 – Comparison of Flux for Different Sodium Metabisulfite Products.

Product		Ventilation Effluent Flow Rate	Total Elapsed Time for Experiment	Time at which maximum flux and SO ₂ concentration identified	Maximum SO ₂ concentration	Minimum Flux	Maximum Flux
		(liters per minute)	(days)	(days)	(ppmv)	(ug m ⁻² s ⁻¹)	
A	Type = sheet Release = dual Use = import Material = plastic	0.3	11	0.8	78.3	0.18	4.38
		0.4	3	0.8	34.5	0.11	2.58
		0.56	2	0.8	28.3	0.37	2.95
	Average		5	0.8	47.0	0.22	3.30
	Standard Deviation		5	0.01	27.3	0.13	0.95
B	Type = sheet Release = dual Use = import Material = plastic	1.3	3	0.64	29.4	0.14	6.87
C	Type = pad Release = dual Use = import Material = paper	2.1	8	2.3	20.3	0.25	7.97
		2.1	14	0.9	24.4	0.58	9.56
		0.85	14	1.5	69.2	0.021	10.98
	Average		12	1.6	38.0	0.28	9.5
	Standard Deviation		3	0.7	27.1	0.28	1.5
D	Type = bag Release = N/A Use = import and export Material = plastic	1.3	10	4.2	38.9	0.01	5.65
		1.3	12	4.9	10.3	0.03	3.55
		2.5	26	3.4	23.6	0.00025	6.58
	Average		16	4.2	24.3	0.013	5.3
	Standard Deviation		9	0.8	14.3	0.015	1.6
E	Type = sheet Release = single Use = export Material = plastic	0.3	5	0.03	5.4	0.00011	0.26
		0.5	4	0.04	1.2	0.02	0.1
		0.5	2	0.04	1	0.00014	0.08
	Average		3	0.04	2.5	0.007	0.15
	Standard Deviation		1.5	0.01	2.5	0.011	0.10
F	Type = pad Release = single Use = Export Material = paper	1	0.7	0.08	14.2	0.23	2.3
		1	0.7	0.0001	33.8	1.21	5.46
		1	0.7	0.08	30.1	2.44	4.87
	Average		0.7	0.1	26.0	1.3	4.2
	Standard Deviation		0	0.05	10.4	1.1	1.7

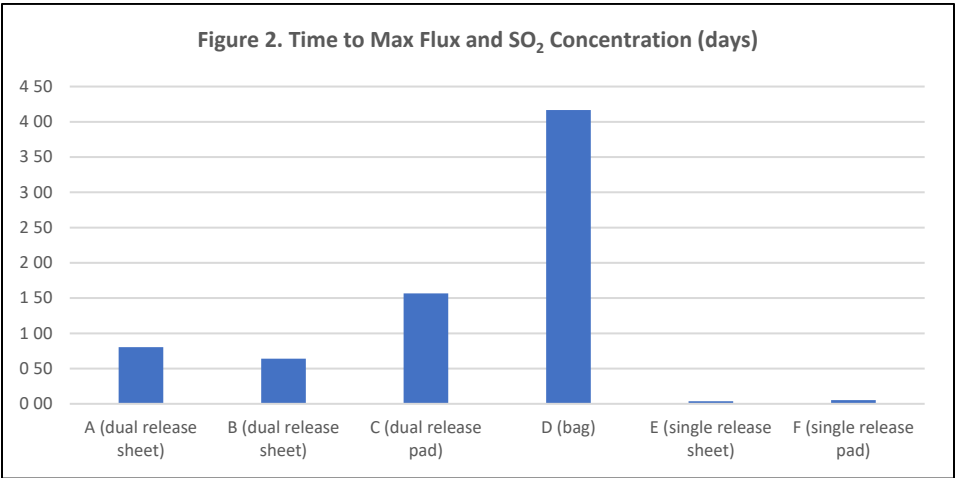
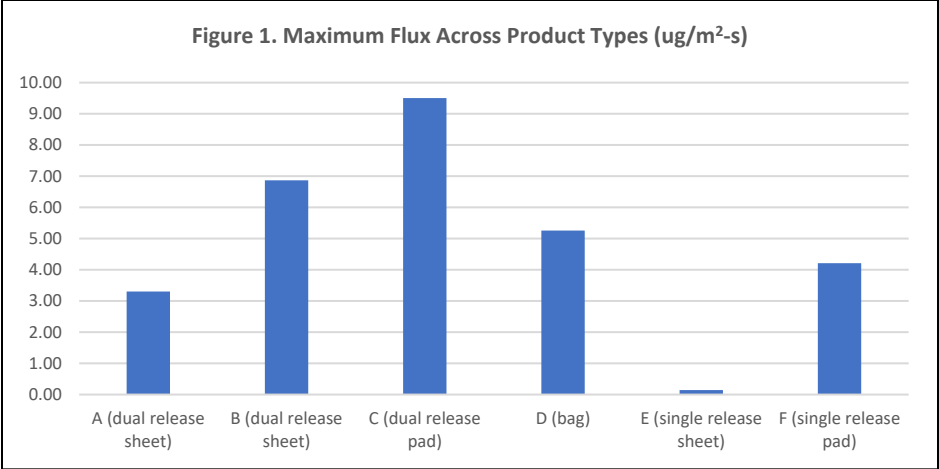


Figure 3. Representative SO₂ Emission Profile – Product A (Dual release)

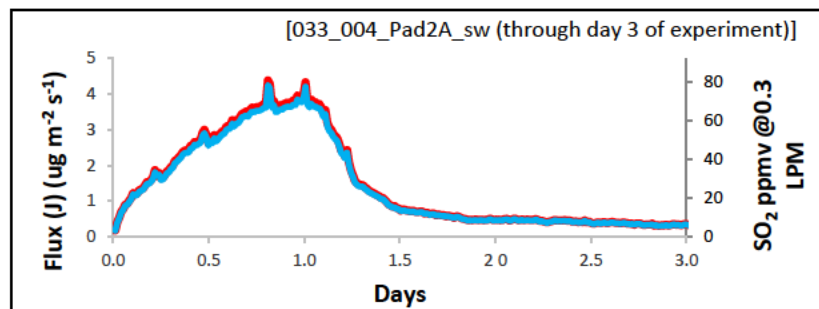


Figure 4. Representative SO₂ Emission Profile – Product B (Dual release)

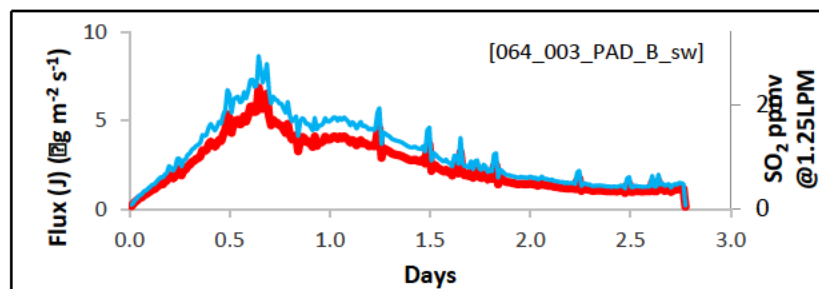


Figure 5. Representative SO₂ Emission Profile – Product C (Dual release)

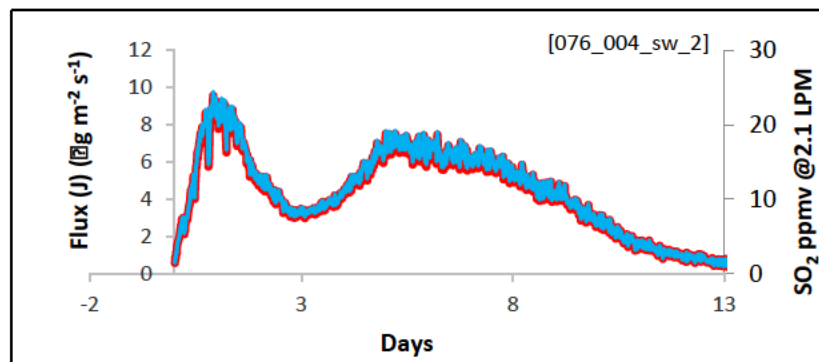


Figure 6. Representative SO₂ Emission Profile – Product D (Bag)

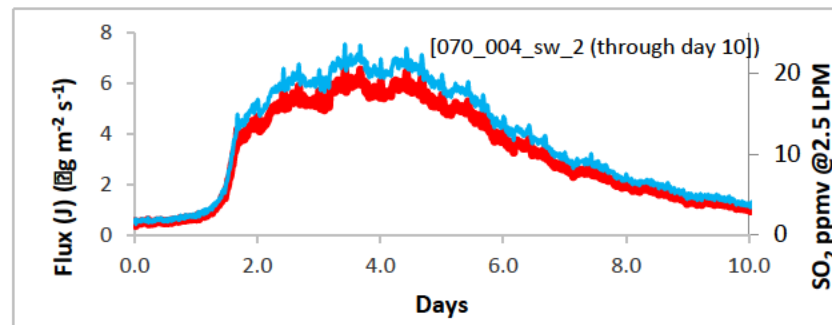


Figure 7. Representative SO₂ Emission Profile – Product E (Single release)

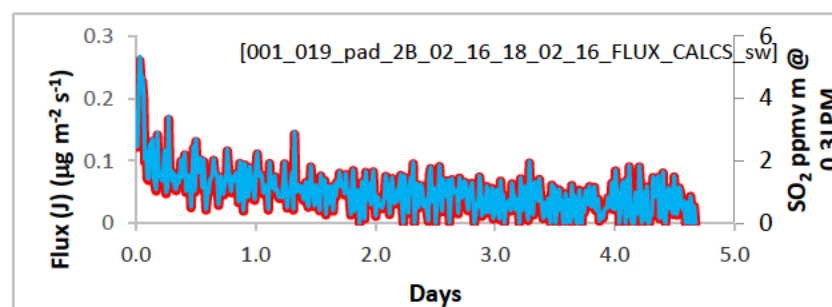


Figure 8. Representative SO₂ Emission Profile – Product F (Single release)

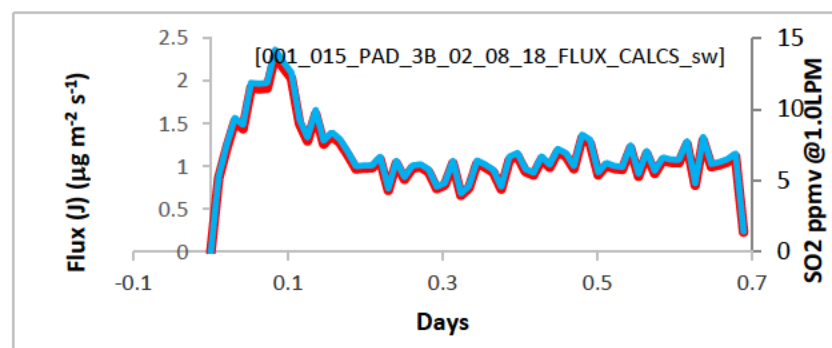


Table 3. Summary of Results for Objective 2: Evaluation of Packing Materials and Grapes on SO₂ Emission From Sodium Metabisulfite Pads.

Scenario		Total Elapsed Time for Experiment	Time at which maximum flux and SO ₂ concentration identified	Max SO ₂		Avg SO ₂ (ppbv)	Avg SO ₂ last 10 days (ppbv)	Max Flux
		(days)		(ppmv)		(ppbv)		(ug m ⁻² s ⁻¹)
Pad only	3 "C" pads only	24	8.2	26.6	26,620	11,326	7,142	0.830
Pad + Boxes (no grapes)	3 "C" pads and 3 boxes (no grapes)	24	11.9	1.83	1,833	268	142	0.057
Pad + Grapes (no boxes)	3 "C" pads and grapes (no boxes)	24	9.9	1.77	1,768	204	94	0.055
Pad + Grapes + Boxes	3 "C" pads, boxes and grapes	24	9.4	1.62	1,615	127	69	0.051

